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THE DETECTION OF SO_3 GAS BY TG/FTIR

by

S.A. Mikhail* and P.E. King**

ABSTRACT

The possibility of identifying SO_3 gas by FTIR was examined. The gas was generated from three different sources and was passed through an FTIR gas cell with conventional KBr windows. Experimental difficulties were encountered and identified. The very high reactivity of SO_3 was a major obstacle in the detection of the gas.

Keywords: TG/FTIR, SO_3, potassium aluminium sulphate, thermogravimetry ir spectra, KBr windows.

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INTRODUCTION

The present work represents an element of an internal project on the development of a solid-state sensor for the continuous and quantitative determination of SO_3/SO_2 gases in process streams. The sensor would ultimately be used in various locations in effluent gas streams and acid-plant absorption towers in non-ferrous smelters and electric power generating plants using sulphur-bearing fuels.

In this work, attempts were made to identify SO_3 gas generated by three different means, namely, solid SO_3 evaporation, sulphuric acid fuming [1,2] and the thermal decomposition of potassium aluminium sulphate hydrate, $KAl(SO_4)_2.12H_2O$. Earlier attempts have been made by Ortigoso et al. [1], Lovejoy et al. [2], Henfrey and Thrush [3] and Sass and Ault [4].

MATERIALS AND EXPERIMENTAL PROCEDURE

Stabilized solid SO_3 (Aldrich Chemicals, 99% purity, m.p. 16.8°C, b.p. 44.7°C), reagent grade H_2SO_4 and $KAl(SO_4)_2.12H_2O$ were used in this work.

The study was done using thermogravimetry and Fourier transform infrared spectroscopy (FTIR). A DuPont TA 9900 thermal analysis system with a 951TGA module was used together with a Bomem MB100 FTIR spectrometer. The thermogravimetry and FTIR techniques were used simultaneously.

RESULTS AND DISCUSSIONS

It is generally known that pure SO_3, in the gaseous, solid or liquid forms, is extremely difficult to handle due to

its very high reactivity with a large variety of materials. The main concerns in this study were as follows:

1. The elimination of moisture from the TG/FTIR system to avoid the reaction of SO_3 forming SO_2 and/or H_2SO_4.

2. The possibility of condensation leading to an attack on the IR cell or internal mirrors.

3. The resolution of SO_3 IR bands. The main band falls in the region 1390 cm^{-1}, which is very close to the SO_2 and H_2O spectral regions.

A small sample of solid SO_3 was transferred quickly from the reagent bottle to an erlenmeyer flask which was continuously purged with a dry inert gas (helium). Some fuming of the sample due to the brief contact with air was noticed. The gas purge was directed to the gas exit system and was continued until the fumes subsided. The SO_3-laden helium was then directed to the FTIR cell and the spectra were collected using a specially developed FTIR macro program:

Shift F10	Learn mode
Shift F5	Name macro
F3	Absorbance
Test#	Name#
5 scans	No. of scans
F1	Execute
ESC	
F10	Menu
F1	Delay
5 s	5 seconds
ESC	
Shift F5	Name macro

Counter macro:

F10	Menu
F2	Set counter
10	Repeat 10 times
20	First test # (name)
ESC	

Shift F5 to start

The spectra were collected using different spectral resolutions, namely, 1, 2 and 4 cm^{-1}. Experiments with resolutions 1 (**Fig. 1**) and 4 (**Fig. 2**) were done at an earlier stage of the study and the resulting spectra were found to be similar and reproducible with no new phases appearing due to the higher resolution technique. The spectra showed bands for SO_2, CO_2 and minor unknown substances. No SO_3 bands were detected. The experiments were repeated using a resolution of 2 cm^{-1} (**Fig. 3**). This time, the spectra indicated the formation of solid products in the FTIR cell and, again, no indication of SO_3. The cell was later examined and, indeed, was found to be covered with a thin layer of deposits which may be the products of reaction between SO_3 and the KBr windows and/or the silver mirrors of the cell.

The second series of experiments were done using the same procedure, with concentrated H_2SO_4 replacing solid SO_3. Two small drops of the liquid were placed in the erlenmeyer flask which was slowly heated in a stream of helium to slightly above the boiling point of H_2SO_4 [1]. After purging to the exhaust for several minutes, the gas was directed to the FTIR cell and the spectral acquisition was initiated (only at 4 cm^{-1} resolution) as explained previously. The obtained spectra, **Fig. 4**, showed the presence of SO_2, S_2O_8 and SO_4^{2-}, with no sign of SO_3 around 1390 cm^{-1}. At the end of this series of experiment, the IR spectrum showed broadening of the bands above 1500 cm^{-1} and the reference spectrum developed an unusual pattern, **Fig. 5**. The long-path cell was dismantled and the reflecting mirrors were found to be covered with a thin white film. Small pits were also found on the surface of the mirrors, most likely due to the corrosive nature of the white substance.

Another series of experiments was done using the simultaneous TG/FTIR equipment and potassium aluminium sulphate hydrate. This compound is known to dehydrate and decompose according to the following scheme [5]:

$$KAl(SO_4)_2.12H_2O = KAl(SO_4)_2 + 12H_2O \quad .....(1)$$

$$2\ KAl(SO_4)_2 = K_2SO_4.Al_2O_3 + 3\ SO_3 \quad .....(2)$$

The complete dehydration (reaction 1) takes place when the compound is heated to about 400°C. The decomposition of the anhydrous product (reaction 2) occurs in the temperature range 700-900°C, depending on the heating rate, with the evolution of SO_3 gas. The starting material was therefore heated in the thermobalance in a helium stream up to 400°C and maintained isothermally for one hour for the complete removal of H_2O. Heating was then continued to 900°C where the sample was maintained isothermally for 30 minutes. The sample mass and the spectra of the effluent gases were monitored during the experiment. The results are presented in **Figure 6** as the change in weight and the gas-evolution profiles of H_2O and SO_2 versus temperature. The weight loss up to 400°C was 44.6% compared to a theoretical weight loss of 45.5% for the dehydration according to reaction 1. The weight loss at high temperature was 25.8% compared to a theoretical loss of 25.7% for the decomposition reaction, 2.

Examination of the IR absorbance of the effluent gas at different temperatures indicated the presence of H_2O (at lower temperatures), SO_2, trace CO_2, and possibly S_2O_8 (815 cm^{-1}), SO_4^{2-} (1091 cm^{-1}) and traces of unknowns. No SO_3 was detected. The sharpness of some of the detected IR bands, **Fig. 7**, can only be due to solid phases, possibly deposited on the KBr windows and/or cell mirrors. In **Figure 8**, the IR spectra of the effluents at 800°C are compared with spectra of SO_2 gas from two different sources.

It is evident that, despite its generation by reaction 2, SO_3 does not reach the FTIR cell. This may be explained on the basis of decomposition of the gas, as it is formed by reaction 2, in the presence of the solid product, $K_2SO_4.Al_2O_3$, acting

as a catalyst. In the presence of a catalyst, SO_3 decomposes to SO_2 and O_2 at temperatures significantly lower than those at which it normally decomposes (>1000^oC) [6].

CONCLUSIONS

Attempts have been made to detect SO_3 gas using FTIR alone and with thermogravimetry (TG/FTIR). The gas was generated from three different sources, each was examined separately. The results showed that it is extremely difficult to detect SO_3 under any of the experimental conditions used. This emphasizes the need for the development of a reliable sensor for this gas, and stresses the importance of the ongoing research work on the project "Development of SO_3/SO_2 sensor" at MSL.

REFERENCES

1. J. Ortigoso, R. Escribano and A.G. Maki, J. Mol. Spectroscopy **138**, 602-613 (1989).

2. R.W. Lovejoy, J.H. Colwell, D.F. Eggers and G.D. Halsey, J. Chem. Phys., **36**(1), 612-617 (1962).

3. N.F. Henfrey and B.A. Thrush, Chem. Phys. Letters, **102**(2,3), 135-138 (1983).

4. C.S. Sass and S. Ault, J. Amer. Chem. Soc., **90**(8), 1547-49 (1986).

5. F. Paulik in "Atlas of thermoanalytical curves", G. Liptay, ed., **2**, 55 (1973).

6. M. Schmitt and W. Siebert, Comprehensive Inorganic Chemistry, **2**, 864 (1973).

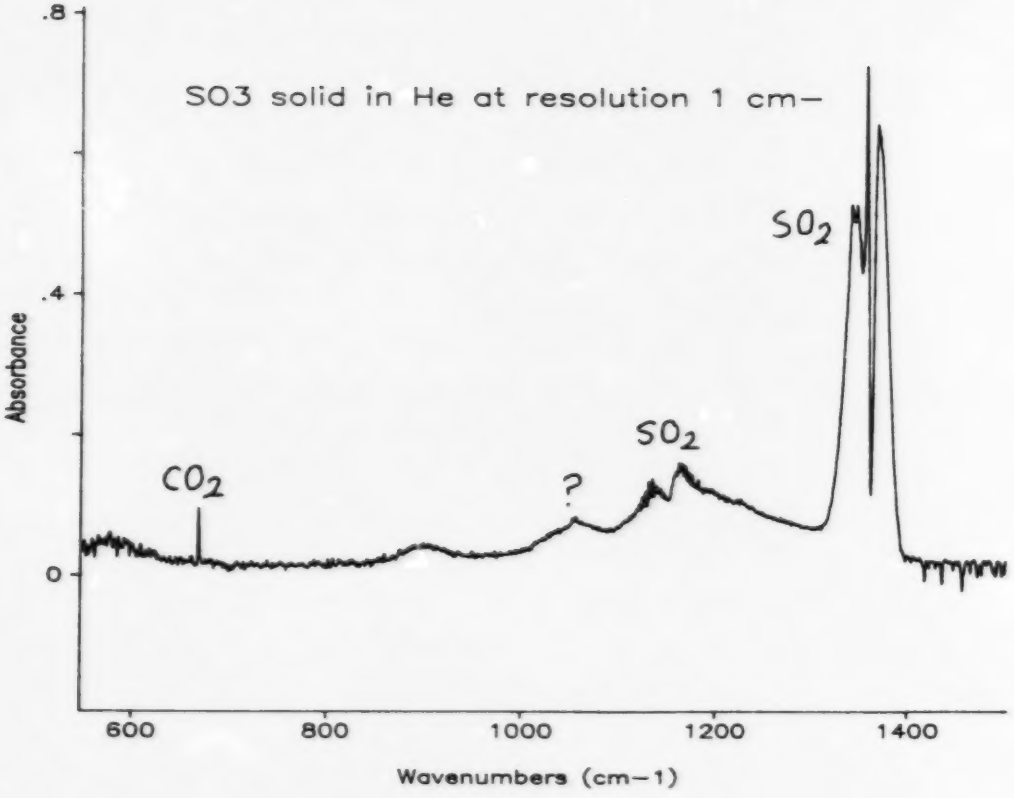

Fig. 1: FTIR absorbance spectrum for gaseous effluents from solid SO_3, 1 cm^{-1} resolution.

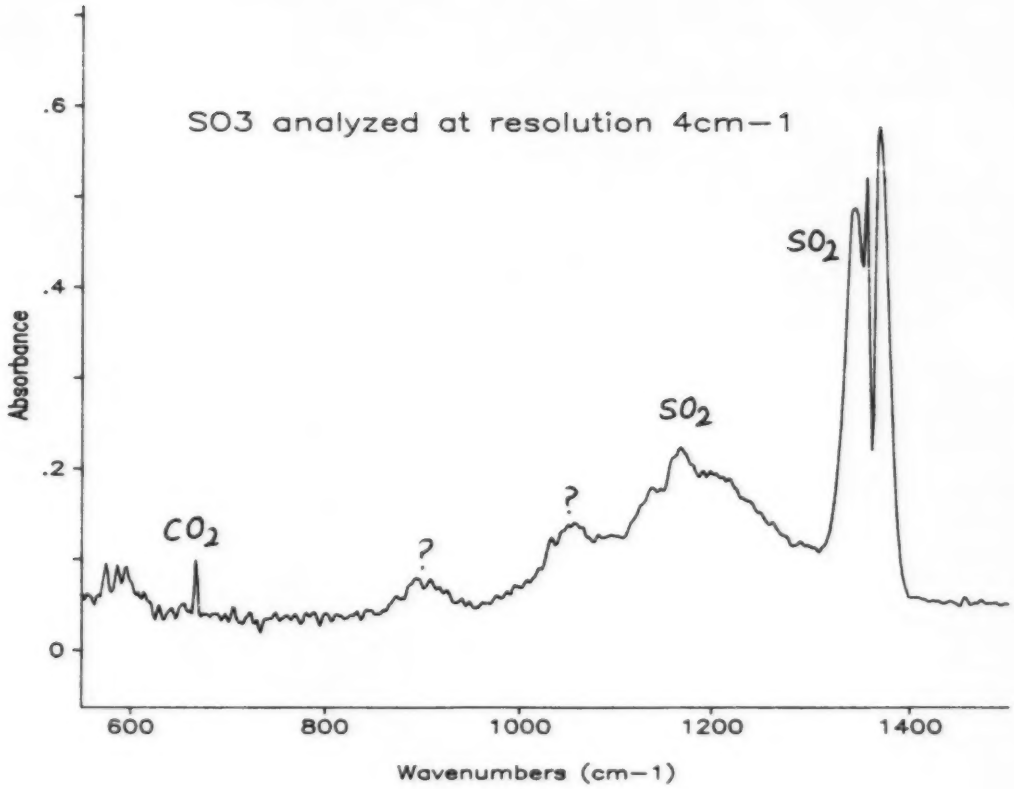

Fig. 2: FTIR absorbance spectrum for gaseous effluents from solid SO_3, 4 cm^{-1} resolution.

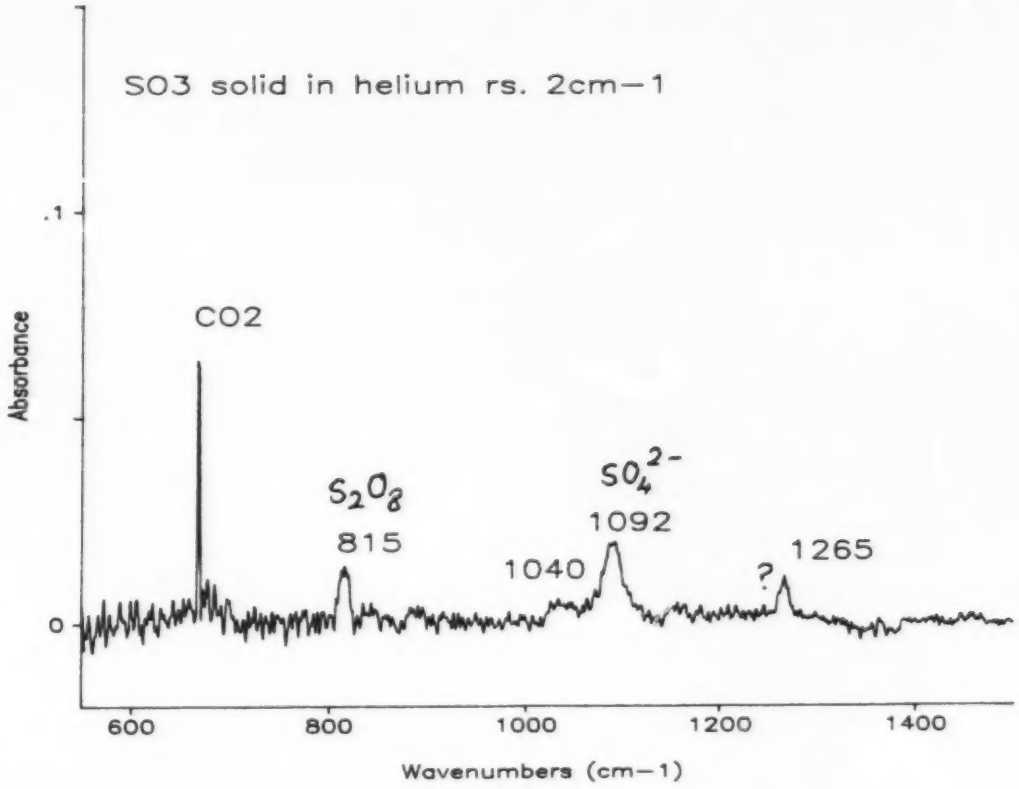

Fig. 3: FTIR absorbance spectrum for gaseous effluents from solid SO_3, 2 cm^{-1} resolution.

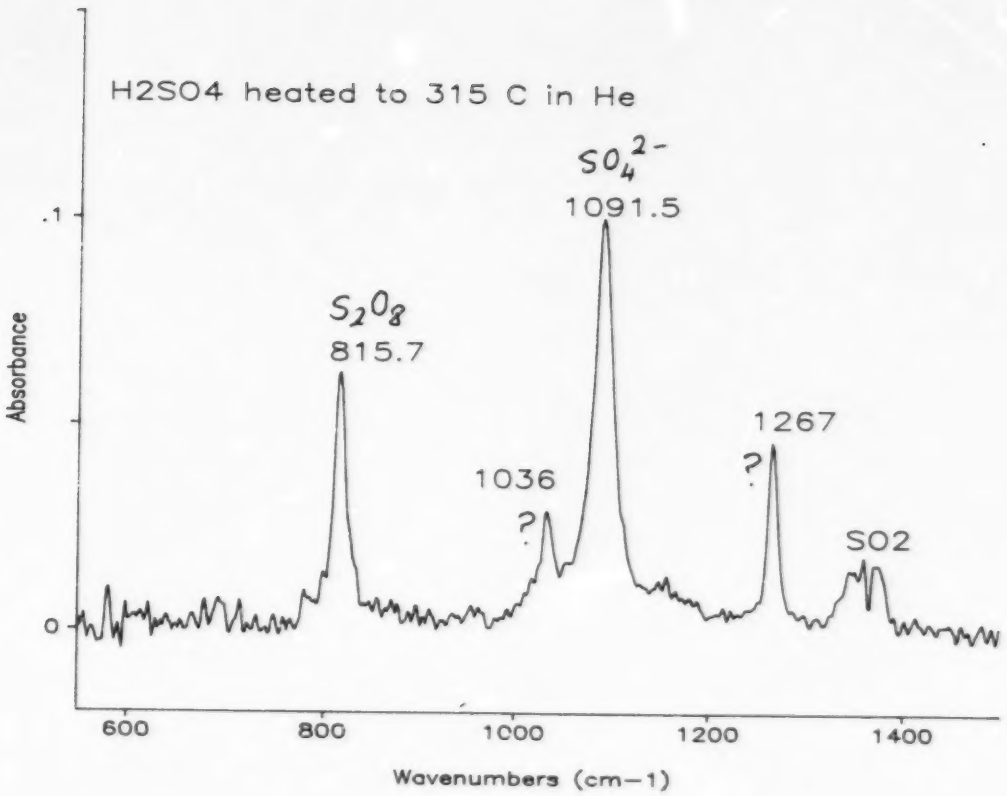

Fig. 4: FTIR absorbance spectrum for gaseous effluents from H_2SO_4 vapour, 4 cm^{-1} resolution.

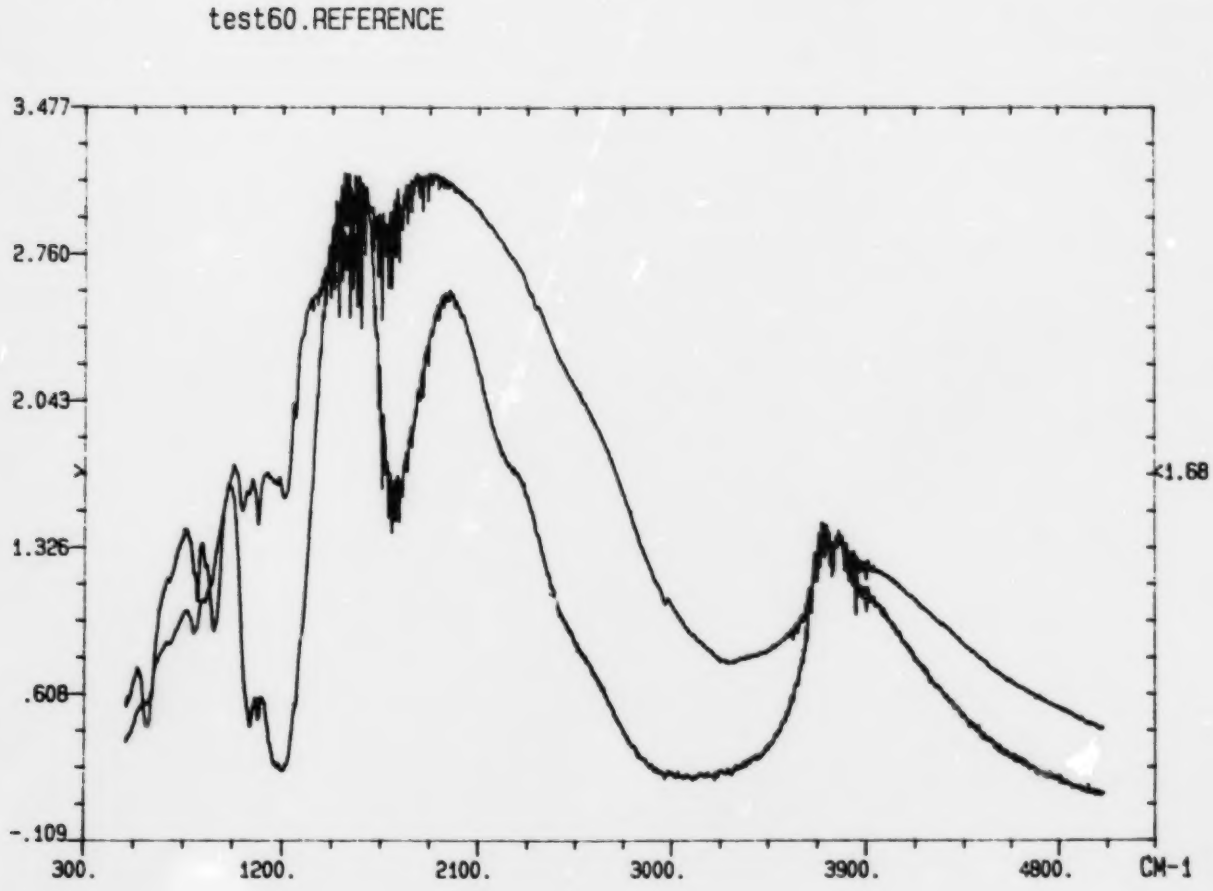

Fig. 5: Reference spectra in nitrogen gas.

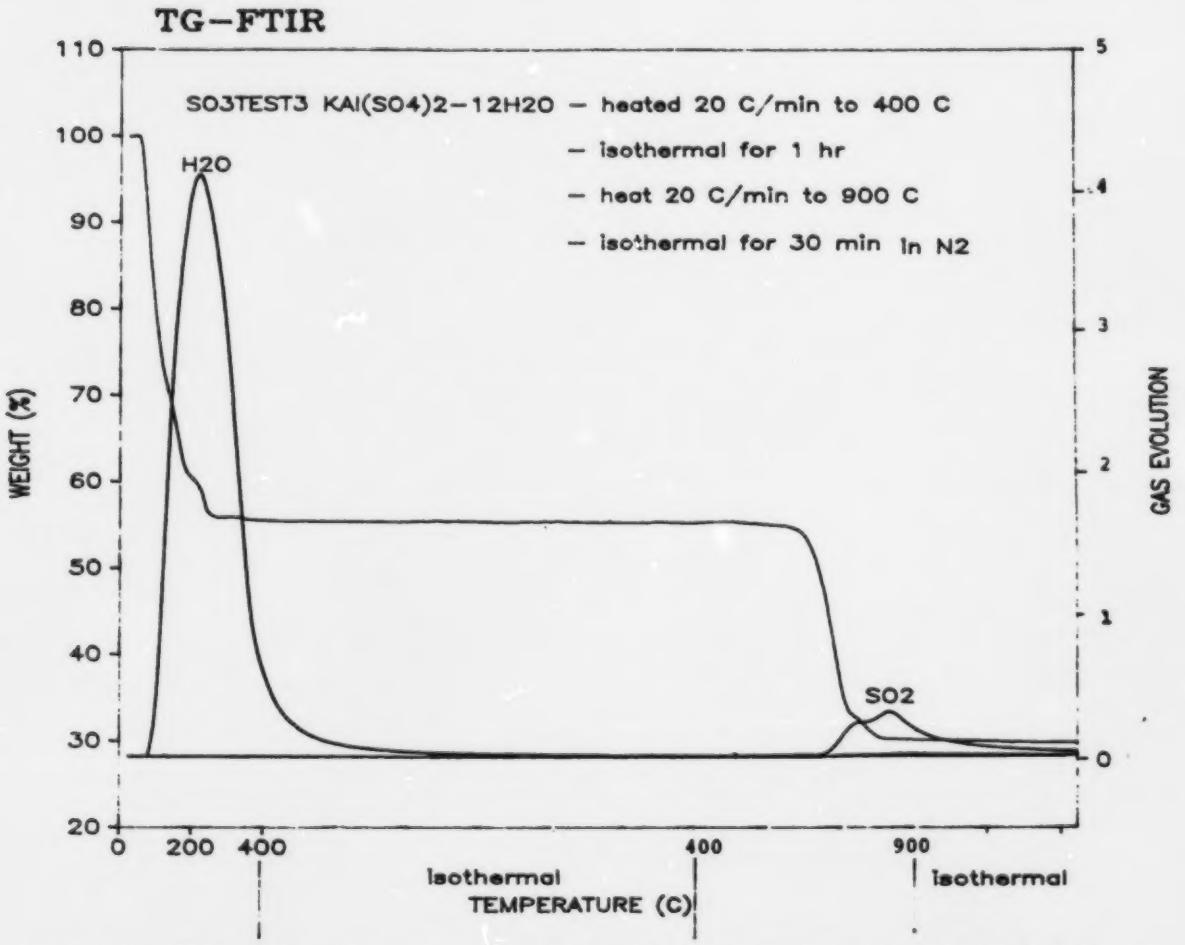

Fig. 6: TG and gas evolution diagrams for potassium aluminium sulphate hydrate in helium.

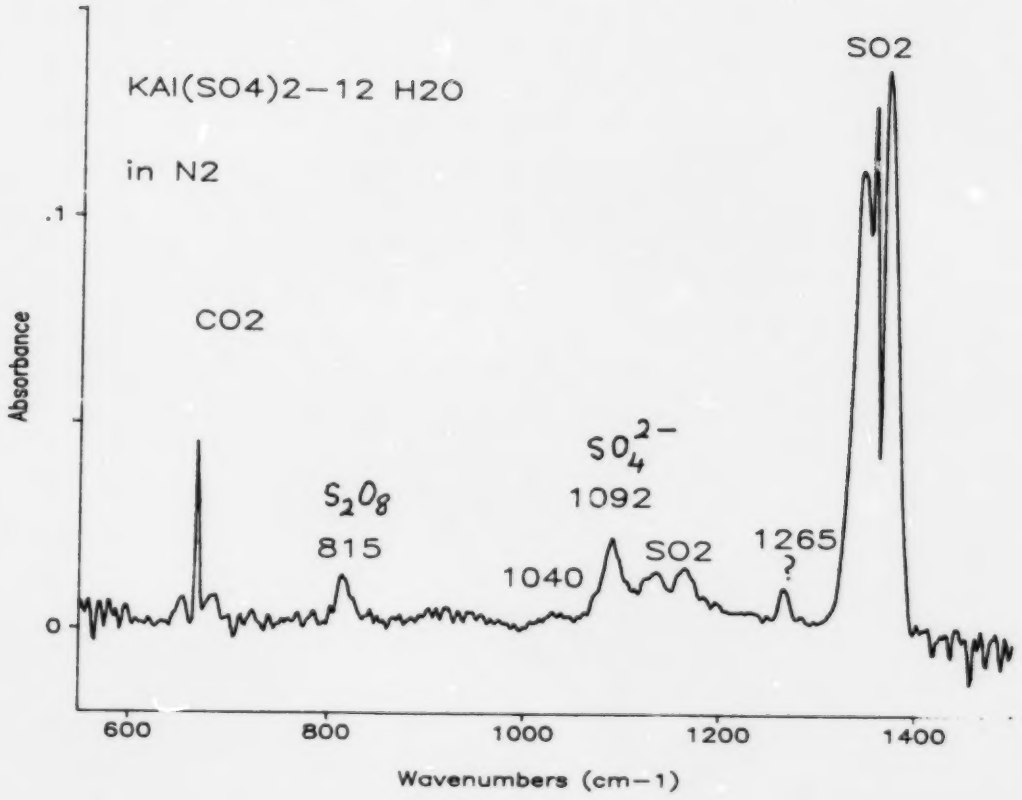

Fig. 7: FTIR spectrum of gaseous effluents from $KAl(SO_4)_2$ at 800°C in nitrogen.

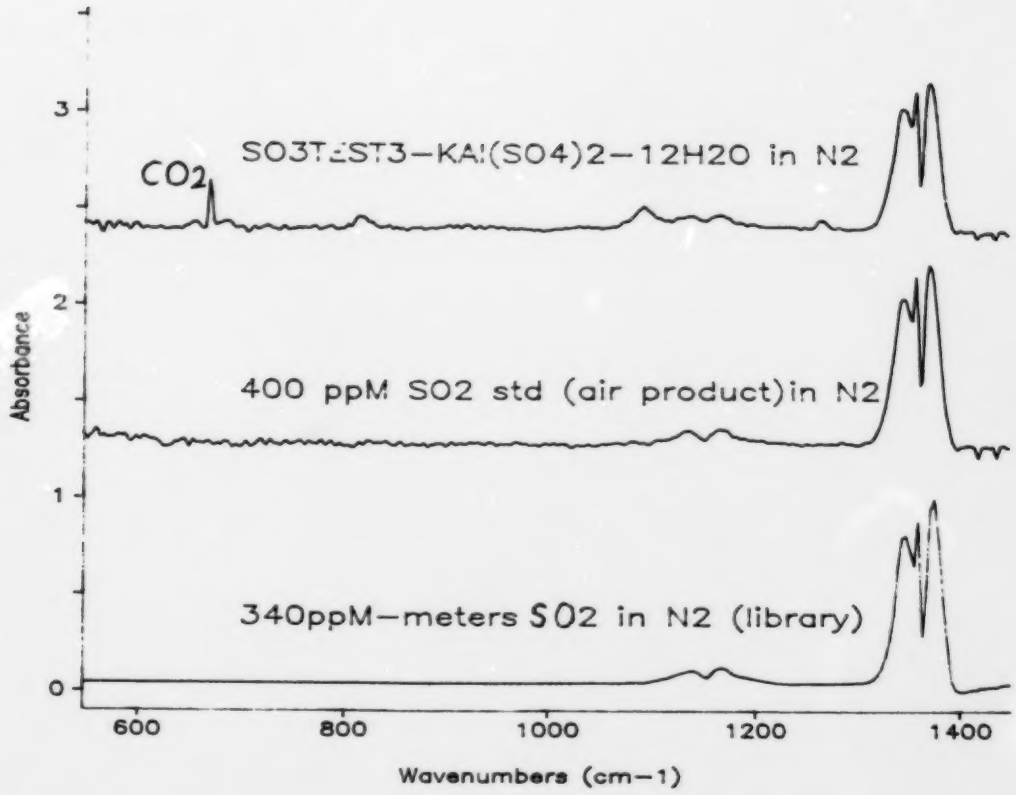

Fig. 8: FTIR spectrum of gaseous effluents from $KAl(SO_4)_2$ at 800°C together with SO_2 spectra from two sources.